

"Nanocrystalline Processing and Interface Engineering of Si<sub>3</sub>N<sub>4</sub>-based Nanocomposites"

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***Nanocrystalline TiN Sintering and Processing***

This quarter's efforts focused on the sintering and processing of nanocrystalline TiN. Lessons learned in working in this system and handling these powders will be invaluable to us in our work with nanocrystalline Si<sub>3</sub>N<sub>4</sub>. Due to its hardness and wear resistance, TiN is potentially very useful in demanding engineering applications. However, due to low sintering activities in microcrystalline powders, TiN has been primarily used as a coating, rather than a monolithic ceramic material. This report outlines processing techniques by which bulk, dense, nanostructured TiN materials may be produced.

As reported in detail previously [1,2], the air-exposed nanocrystalline TiN produced in our novel reactor undergoes tremendous sintering and densification to produce TiN materials which are ~95% dense. The commercial TiN materials processed identically to our nano-TiN sintered to a much lower density (65%) with very large grain sizes ( $\geq 10 \mu\text{m}$ ). While this work demonstrated the enhanced sinterabilities of our nanocrystalline powders, the need to address the oxidation tendencies of nano-nitrides was also shown very clearly. As the air-exposed TiN was sintered, a Ti<sub>3</sub>O<sub>5</sub> phase was crystallized. This phase is first detected by XRD at 1200 °C and has developed appreciably by 1600 °C. While some amount of this Ti<sub>3</sub>O<sub>5</sub> is likely present at the grain boundaries, SEM revealed the development of a segregated second phase at 1200 °C. At 1400 °C, a significant amount of this second phase is developed and is shown by EDAX to be enriched in O<sub>2</sub> relative to the primary TiN phase. It seems likely that the large amount of O<sub>2</sub> present on these powders (due to their extremely high surface areas) segregates and crystallizes into this Ti<sub>3</sub>O<sub>5</sub> phase at elevated temperatures. As this phase has a lower density (~4.10 g/cm<sup>3</sup>) than TiN, the overall theoretical density of these materials is lowered. Additionally, substantial cracking at the phase interfaces, likely due to thermal and lattice mismatch between the two phases, occurs at 1400 °C. Other work on nano-TiN has also demonstrated the development of small amounts of an O<sub>2</sub>-rich second phase upon sintering [3], but our results, due to our higher surface area powder, demonstrate very clearly the oxidation challenge that must be overcome for the successful utilization of high quality, nanocrystalline nitride materials.

Based on the results of this study, a valved filter collection device was added to the reactor to allow powder removal without exposure to air. Particles are deposited on a porous metal filter mounted perpendicular to the gas stream inside the reactor. Following a synthesis run, the reactor is backfilled with high purity N<sub>2</sub> and gate valves are closed to allow the filter collection unit to be removed from the reactor and placed into a glovebox (H<sub>2</sub>O < 1 ppm, O<sub>2</sub> < 1 ppm) for powder removal. The particles are removed from the filter collection unit under a high purity Ar atmosphere in the glovebox and are uniaxially pressed

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(200 MPa) in an evacuable pellet die. The formed pellets are then removed from the die in the glovebox and sealed in bags for cold isostatic pressing (CIP) (300 MPa). Following the CIP procedure, the pellets are returned to the glovebox, unsealed from their bags and transferred directly to a furnace connected to the glovebox for pre-sintering. The pellets are ramped under flowing N<sub>2</sub> at 2 °C/min to 800 °C to allow sintering to take place with a resultant reduction in surface area before the materials are ever exposed to air. At this point, the pellets are briefly (~15 seconds) exposed to air as they are transferred to the high temperature furnace for final sintering (0.1 MPa overpressure of N<sub>2</sub>, ramped at 2 °C/min to the sintering temperature with a 30 minute soak).

These careful powder handling procedures allowed us to produce dense (99%), nanostructured (grain size ≈ 250 nm) TiN through this pressureless sintering process at 1400 °C. A key to this successful processing is that the unexposed powders had an undetectable (0%) weight loss during sintering, while the air-exposed powders, due to the moisture and oxygen absorbed during exposure, had a very large weight loss (16%) during sintering. There were no large second phase regions or porosity visible in the unexposed nano-TiN materials when examined via SEM. These results are particularly noteworthy due to the processing conditions which had been required by others to produce similarly dense TiN materials. Previous efforts by other researchers with lower quality starting powders required high applied gas pressures (5 MPa N<sub>2</sub>) [3] or high applied compaction pressures (4 GPa) [4] to achieve comparable densities. Our on-going research involves studying the effects of pressure-assisted consolidation processes to reduce further the final grain sizes in the nano-TiN and the evaluation of the properties (hardness, electrical conductivity, etc.) of these unique nano-nitrides. We are also exploring the potential for removing the surface oxide layer on the air-exposed TiN powders via pre-sintering processing.

### **Summary**

A new filter collection unit on our reactor and careful powder handling procedures allowed us to produce dense (99%), nanostructured (grain size ≈ 250 nm) TiN through a pressureless sintering process at 1400 °C.

### **References**

1. J.Y. Ying, ONR Technical Report, June 30, 1996.
2. D.T. Castro and J.Y. Ying, "Synthesis and Sintering of Nanocrystalline Titanium Nitride," submitted to *Nanostructured Materials*.
3. T. Rabe and R. Wäsche, *Ceram. Trans.* **51**, 793-798 (1995).
4. R.A. Andrievski, *ACS Symposium Series*, **622**, 294-301 (1996).

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